

What is claimed is:

1. A composite polymer electrolyte membrane comprising a mixture of at least two types of polymer electrolyte including a first polymer electrolyte and a second polymer electrolyte, wherein:

the first polymer electrolyte comprises a sulfonated polyarylene polymer, while the second polymer electrolyte comprises a hydrocarbon polymer sulfonate other than a sulfonated polyarylene polymer.

2. A composite polymer electrolyte membrane according to claim 1, wherein the first polymer electrolyte constitutes 50-95 wt% of the whole membrane.

3. A composite polymer electrolyte membrane according to claim 1, wherein the first polymer electrolyte comprises a sulfonated polyarylene polymer whereof 2-70 mol% comprises an aromatic compound unit with an electron-attractive group in its principal chain, and 30-98 mol% comprises an aromatic compound unit without an electron-attractive group in its principal chain.

4. A composite polymer electrolyte membrane according to claim 3, wherein the electron-attractive group comprises one or more bivalent electron-attractive groups selected from among -CO-, -CONH-, $-(CF_2)_p-$ (where p is an integer between 1 and 10), $-C(CF_3)_2-$, -COO-, -SO- and -SO₂-.

5. A composite polymer electrolyte membrane according to claim 3, wherein the first polymer electrolyte constitutes 70-95 wt% of the whole membrane.

6. A composite polymer electrolyte membrane according to claim 3, wherein the first polymer electrolyte comprises a sulfonated polyarylene polymer whereof 7-35 mol% comprises an aromatic compound unit having a benzophenone-4,4'-diyl structure as the aromatic compound unit with an electron-attractive group in its principal chain, and 65-93 mol% comprises an aromatic compound unit having a 4'-phenoxybenzophenone-2,5-diyl structure as the aromatic compound unit without an electron-attractive group in its principal chain.

7. A composite polymer electrolyte membrane according to claim 6, wherein the sulfonated polyarylene polymer has an ion exchange capacity of 1.5-3.0 meq/g.

8. A composite polymer electrolyte membrane according to claim 3, wherein the first polymer electrolyte comprises a sulfonated polyarylene polymer whereof 3-60 mol% comprises an aromatic compound unit having at least one structure wherein the aromatic compounds are ether-bonded as the aromatic compound unit with an electron-attractive group in its principal chain, and 40-97 mol% comprises an aromatic compound unit without an electron-attractive group in its principal

chain.

9. A composite polymer electrolyte membrane according to claim 8, wherein the first polymer electrolyte comprises a sulfonated polyarylene polymer whereof 3-60 mol% comprises an aromatic compound unit having a bis(benzoyl)diphenylether-4,4'-diyl structure as the aromatic compound unit with an electron-attractive group in its principal chain, and 40-97 mol% comprises an aromatic compound unit having a 4'-phenoxy-benzophenone-2,5-diyl structure as the aromatic compound unit without an electron-attractive group in its principal chain.

10. A composite polymer electrolyte membrane according to claim 9, wherein the sulfonated polyarylene polymer has an ion exchange capacity of 1.5-3.0 meq/g.

11. A composite polymer electrolyte membrane according to claim 1, wherein the second polymer electrolyte comprises a sulfonated polyether or sulfonated polysulfide polymer electrolyte.

12. A composite polymer electrolyte membrane according to claim 11, wherein the second polymer electrolyte comprises one or more polymer electrolytes selected from among sulfonated polyphenylene oxides, sulfonated polyether ether ketones and sulfonated polyphenylene sulfides.

13. A solid polymer electrolyte fuel cell equipped with an

membrane electrode assembly wherein a pair of electrodes and an electrolyte membrane between the two electrodes are combined so as to form a single entity, wherein:

the electrolyte membrane comprises a composite polymer electrolyte membrane comprising a mixture of at least two types of polymer electrolyte including a first polymer electrolyte and a second polymer electrolyte, the first polymer electrolyte comprising a sulfonated polyarylene polymer, while the second polymer electrolyte comprises a hydrocarbon polymer sulfonate other than a sulfonated polyarylene polymer.

14. A composite polymer electrolyte membrane comprising a mixture of at least two types of polymer electrolyte including a first polymer electrolyte and a second polymer electrolyte, comprising:

a matrix comprising a first polymer electrolyte selected from among polyarylene polymer sulfonates and having an ion exchange capacity of at least 1.5 meq/g but less than 3.0 meq/g; and

a reinforcement comprising a second polymer electrolyte selected from among sulfonated polyarylene polymers and having an ion exchange capacity of at least 0.5 meq/g but less than 1.5 meq/g;

wherein the matrix being retained by the reinforcement.

15. A composite polymer electrolyte membrane according to claim 14, wherein the ion exchange capacity of the polyarylene polymers sulfonate which constitutes the matrix is at least 1.7 meq/g but less than 2.5 meq/g, while that of the sulfonated polyarylene polymer which constitutes the reinforcement is at least 0.5 meq/g but less than 1.3 meq/g.

16. A composite polymer electrolyte membrane according to claim 15, wherein the first and second polymer electrolyte comprise a sulfonated polyarylene polymer whereof 5-70 mol% comprises an aromatic compound unit with an electron-attractive group in its principal chain, and 30-95 mol% comprises an aromatic compound unit without an electron-attractive group in its principal chain.

17. A composite polymer electrolyte membrane according to claim 16, wherein the molar ratio of aromatic units in the polyarylene polymer of the sulfonated polyarylene polymer which forms the matrix is different from the molar ratio of aromatic units in the polyarylene polymer of the sulfonated polyarylene polymer which forms the reinforcement.

18. A composite polymer electrolyte membrane according to claim 16, wherein while the molar ratio of aromatic units in the polyarylene polymers of the sulfonated polyarylene polymers which form the matrix and the reinforcement are the same, the polyarylene polymers are sulfonated under different

conditions.

19. A composite polymer electrolyte membrane according to claim 16, wherein the electron-attractive group comprises one or more bivalent electron-attractive groups selected from among -CO- , -CONH- , $\text{-(CF}_2\text{)}_p\text{-}$ (where p is an integer between 1 and 10), $\text{-C(CF}_3\text{)}_2\text{-}$, -COO- , -SO- and $\text{-SO}_2\text{-}$.

20. A composite polymer electrolyte membrane according to claim 16, wherein the sulfonated polyarylene polymers which constitute the matrix and reinforcement comprise sulfonates except for sulfonates having a perfluoroalkylene in part of a substitution group or in part of the principal chain structure.

21. A composite polymer electrolyte membrane according to claim 20, wherein the sulfonated polyarylene polymers which constitute the matrix and reinforcement comprise sulfonated polyarylene polymers whereof 7-35 mol% comprises an aromatic compound unit having a benzophenone-4,4'-diyl structure as the aromatic compound unit with an electron-attractive group in its principal chain, and 65-93 mol% comprises an aromatic compound unit having a 4'-phenoxy-benzophenone-2,5-diyl structure as the aromatic compound unit without an electron-attractive group in its principal chain.

22. A composite polymer electrolyte membrane according to claim 21, wherein the sulfonated polyarylene polymer has an

ion exchange capacity of at least 0.5 meq/g but less than 3.0 meq/g.

23. A composite polymer electrolyte membrane according to claim 20, wherein the sulfonated polyarylene polymers which constitute the matrix and reinforcement comprise sulfonated polyarylene polymers whereof 3-40 mol% comprises an aromatic compound unit having at least one structure wherein the aromatic compounds are ether-bonded as the aromatic compound unit with an electron-attractive group in its principal chain, and 60-97 mol% comprises an aromatic compound unit without an electron-attractive group in its principal chain.

24. A composite polymer electrolyte membrane according to claim 23, wherein the sulfonated polyarylene polymers which constitute the matrix and reinforcement comprise sulfonated polyarylene polymers whereof 3-40 mol% comprises an aromatic compound unit having a bis(benzoyl)diphenylether-4,4'-diyl structure as the aromatic compound unit with an electron-attractive group in its principal chain, and 60-97 mol% comprises an aromatic compound unit having a 4'-phenoxy-benzophenone-2,5-diyl structure as the aromatic compound unit without an electron-attractive group in its principal chain.

25. A composite polymer electrolyte membrane according to claim 24, wherein the sulfonated polyarylene polymer has an

ion exchange capacity of at least 0.5 meq/g but less than 3.0 meq/g.

26. A composite polymer electrolyte membrane according to claim 14, wherein the sulfonated polyarylene polymer which constitutes the reinforcement is in the form of fibers.

27. A composite polymer electrolyte membrane according to claim 14, wherein the sulfonated polyarylene polymer which constitutes the reinforcement is in the form of a porous film.

28. A method of manufacturing a composite polymer electrolyte membrane comprising:

a process of selecting a sulfonate matrix having an ion exchange capacity of at least 1.5 meq/g but less than 3.0 meq/g from among sulfonated polyarylene polymers whereof 5-70 mol% comprises an aromatic compound unit with an electron-attractive group in its principal chain, and 30-95 mol% comprises an aromatic compound unit without an electron-attractive group in its principal chain, and dissolving the matrix in a solvent to produce a uniform matrix solution,

a process of selecting a sulfonate reinforcement in the form of fibers having an ion exchange capacity of at least 0.5 meq/g but less than 1.5 meq/g from among sulfonated polyarylene polymers whereof 5-70 mol% comprises an aromatic compound unit with an electron-attractive group in its principal chain, and 30-95 mol% comprises an aromatic compound unit without an

electron-attractive group in its principal chain, and dispersing the reinforcement in the matrix solution to produce a uniform slurry, and

a process of drying the slurry in sheet form.

29. A method of manufacturing a composite polymer electrolyte membrane comprising:

a process of selecting a sulfonate matrix having an ion exchange capacity of at least 1.5 meq/g but less than 3.0 meq/g from among sulfonated polyarylene polymers whereof 5-70 mol% comprises an aromatic compound unit with an electron-attractive group in its principal chain, and 30-95 mol% comprises an aromatic compound unit without an electron-attractive group in its principal chain, and dissolving the matrix in a solvent to produce a uniform matrix solution,

a process of selecting a sulfonate reinforcement having an ion exchange capacity of at least 0.5 meq/g but less than 1.5 meq/g from among sulfonated polyarylene polymers whereof 5-70 mol% comprises an aromatic compound unit with an electron-attractive group in its principal chain, and 30-95 mol% comprises an aromatic compound unit without an electron-attractive group in its principal chain, and dissolving the reinforcement in a solvent to produce a uniform reinforcement solution,

a process of preparing a reinforcement in the form of a porous

film from the reinforcement solution, and

a process of impregnating the reinforcement in the form of a porous film with the matrix solution.

30. A solid polymer electrolyte fuel cell equipped with an membrane electrode assembly wherein a pair of electrodes and an electrolyte membrane between the two electrodes are combined so as to form a single entity, wherein:

the electrolyte membrane comprises a composite polymer electrolyte membrane comprising a mixture of at least two types of polymer electrolyte including a first polymer electrolyte and a second polymer electrolyte, being formed of a matrix comprising a first polymer electrolyte selected from among sulfonated polyarylene polymer and having an ion exchange capacity of at least 1.5 meq/g but less than 3.0 meq/g, and a reinforcement comprising a second polymer electrolyte selected from among sulfonated polyarylene polymers and having an ion exchange capacity of at least 0.5 meq/g but less than 1.5 meq/g, the matrix being retained by the reinforcement.

31. An membrane electrode assembly comprises a pair of electrodes and an electrolyte membrane between the two electrodes are combined so as to form a single entity, wherein:

the electrolyte membrane comprises a polymer electrolyte membrane comprising a sulfonated polyarylene polymer which

in turn comprises an aromatic compound unit with an electron-attractive group in its principal chain, and an aromatic compound unit without an electron-attractive group in its principal chain,

the polyarylene polymer being sulfonated in such a manner that, an electrode containing a 0.5 mg/cm^2 platinum catalyst being located on one surface of the polymer electrolyte membrane, if the surface of the polymer electrolyte membrane on the side opposite to the electrode is brought into contact with an aqueous solution of sulfuric acid having a pH value of 1 and nitrogen gas is delivered to the electrode in such a manner that the voltage impressed between the aqueous solution of sulfuric acid and the electrode changes continuously from -0.1 to 0.7 volts, the electric charge per unit area represented as a value obtained by dividing the peak area on the proton adsorption side by the area of the membrane electrode assembly is within the range $0.09\text{--}0.18 \text{ C/cm}^2$.

32. An membrane electrode assembly according to claim 31, wherein the polymer electrolyte membrane comprises a sulfonated polyarylene polymer whereof 5-70 mol% comprises an aromatic compound unit with an electron-attractive group in its principal chain, and 30-95 mol% comprises an aromatic compound unit without an electron-attractive group in its principal chain.

33. An membrane electrode assembly according to claim 31, wherein the electron-attractive group comprises one or more bivalent electron-attractive groups selected from among -CO-, -CONH-, $-(CF_2)_p-$ (where p is an integer between 1 and 10), $-C(CF_3)_2-$, -COO-, -SO- and -SO₂-.

34. An membrane electrode assembly according to claim 31, wherein the sulfonated polyarylene polymer which constitutes the polymer electrolyte film except for sulfonates having a perfluoroalkylene in part of a substitution group or in part of the principal chain structure.

35. An membrane electrode assembly according to claim 34, wherein the sulfonated polyarylene polymers which constitute the polymer electrolyte membrane comprises sulfonated polyarylene polymers whereof 7-35 mol% comprises an aromatic compound unit having a benzophenone-4,4'-diyl structure as the aromatic compound unit with an electron-attractive group in its principal chain, and 65-93 mol% comprises an aromatic compound unit having a 4'-phenoxy-benzophenone-2,5-diyl structure as the aromatic compound unit without an electron-attractive group in its principal chain.

36. An membrane electrode assembly according to claim 35, wherein the sulfonated polyarylene polymer has an ion exchange capacity of 1.5-3.0 meq/g.

37. An membrane electrode assembly according to claim 35,

wherein the sulfonated polyarylene polymer which constitutes the polymer electrolyte membrane comprises a sulfonated polyarylene polymer whereof 3-60 mol% comprises an aromatic compound unit having at least one structure wherein the aromatic compounds are ether-bonded as the aromatic compound unit with an electron-attractive group in its principal chain, and 40-97 mol% comprises an aromatic compound unit without an electron-attractive group in its principal chain.

38. An membrane electrode assembly according to claim 37, wherein the sulfonated polyarylene polymers which constitute the polymer electrolyte membrane comprises sulfonated polyarylene polymers whereof 3-40 mol% comprises an aromatic compound unit having a bis(benzoyl)diphenylether-4,4'-diyl structure as the aromatic compound unit with an electron-attractive group in its principal chain, and 60-97 mol% comprises an aromatic compound unit having a 4'-phenoxy-benzophenone-2,5-diyl structure as the aromatic compound unit without an electron-attractive group in its principal chain.

39. An membrane electrode assembly according to claim 37, wherein the sulfonated polyarylene polymer has an ion exchange capacity of 1.5-3.0 meq/g.

40. A solid polymer electrolyte fuel cell equipped with an membrane electrode assembly wherein a pair of electrodes and

an electrolyte membrane between the two electrodes are combined so as to form a single entity, wherein:

the electrolyte membrane comprises a polymer electrolyte membrane whereof 5-70 mol% comprises an aromatic compound unit with an electron-attractive group in its principal chain, and 30-95 mol% comprises an aromatic compound unit without an electron-attractive group in its principal chain,

the polyarylene polymer being sulfonated in such a manner that, an electrode containing a 0.5 mg/cm^2 platinum catalyst being located on one surface of the polymer electrolyte membrane, if the surface of the polymer electrolyte membrane on the side opposite to the electrode is brought into contact with an aqueous solution of sulfuric acid having a pH value of 1 and nitrogen gas is delivered to the electrode in such a manner that the voltage impressed between the aqueous solution of sulfuric acid and the electrode changes continuously from -0.1 to 0.7 volts, the electric charge per unit area represented as a value obtained by dividing the peak area on the proton adsorption side by the area of the membrane electrode assembly is within the range $0.09-0.18 \text{ C/cm}^2$.